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<b>(21) International Application Number:</b> PCT/GB00/00079 <b>(22) International Filing Date:</b> 17 January 2000 (17.01.00) <b>(30) Priority Data:</b> 9901413.6                      23 January 1999 (23.01.99)                      GB <b>(71) Applicant (for all designated States except US):</b> AEA TECHNOLOGY PLC [GB/GB]; 329 Harwell, Didcot, Oxfordshire OX11 0RA (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> RAYBONE, David [GB/GB]; 1 Talbot Cottages, Fosse Way, Stow-on-the-Wold, Gloucester GL54 1DW (GB). SEGAL, David, Leslie [GB/GB]; 43 Foxborough Road, Radley, Abingdon, Oxfordshire OX14 3AB (GB). SHAWCROSS, James, Timothy [GB/GB]; 27 Ticknell Piece Road, Charlbury, Oxfordshire OX7 3TN (GB). <b>(74) Agents:</b> LOFTING, Marcus, John et al.; AEA Technology plc, Patents Dept., 329 Harwell, Didcot, Oxfordshire OX11 0RA (GB).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> REACTOR FOR PLASMA ASSISTED GAS PROCESSING  <b>(57) Abstract</b>  A process and apparatus for the treatment of internal combustion engine exhaust gases in which a non-thermal plasma is used to promote the removal of particulate carbonaceous emissions via the oxidation of NO to NO <sub>2</sub> and its subsequent reaction with the particulates.		

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Reactor for Plasma Assisted Gas Processing

The present invention relates to reactors for the plasma-assisted processing of gaseous media and in particular to plasma assisted catalytic reactors for the reduction of the emission of carbonaceous and nitrogenous oxide combustion products from the exhausts of internal combustion engines.

One of the major problems associated with the development and use of internal combustion engines is the noxious exhaust emissions from such engines. Two of the most undesirable materials, particularly in the case of diesel engines, are particulate matter (primarily carbon) and oxides of nitrogen ( $\text{NO}_x$ ). Increasingly severe emission control regulations are forcing internal combustion engine and vehicle manufacturers to find more efficient ways of removing these materials in particular from internal combustion engine exhaust emissions. Unfortunately, in practice, it is found that combustion modification techniques which improve the situation in relation to one of the above components of internal combustion engine exhaust emissions tend to worsen the situation in relation to the other. Even so, a variety of systems for trapping particulate emissions from internal combustion engine exhausts have been investigated, particularly in relation to making such particulate emission traps capable of being regenerated when they have become saturated with particulate material.

Examples of such diesel exhaust particulate filters are to be found in European patent applications EP 0 010 384; US patents 4,505,107; 4,485,622; 4,427,418; and 4,276,066; EP 0 244 061; EP 0 112 634 and EP 0 132 166.

- 2 -

In all the above cases, the particulate matter is removed from diesel exhaust gases by a simple, physical trapping of particulate matter in the interstices of a porous, usually ceramic, filter body, which is then  
5 regenerated by heating the filter body to a temperature at which the trapped diesel exhaust particulates are burnt off. In most cases the filter body is monolithic, although EP 0 010 384 does mention the use of ceramic beads, wire meshes or metal screens as well. US patent  
10 4,427,418 discloses the use of ceramic coated wire or ceramic fibres.

In a broader context, the precipitation of charged particulate matter by electrostatic forces also is known.  
15 However, in this case, precipitation usually takes place upon large planar electrodes or metal screens.

GB patent 2,274,412 discloses a method and apparatus for removing particulate and other pollutants from  
20 internal combustion engine exhaust gases, in which the exhaust gases are passed through a bed of charged pellets of material, preferably ferroelectric, having high dielectric constant. In addition to removing particulates by oxidation, especially electric discharge  
25 assisted oxidation, there is disclosed the reduction of NO<sub>x</sub> gases to nitrogen, by the use of pellets adapted to catalyse the NO<sub>x</sub> reduction.

Cooper et al in a paper entitled 'Role of NO in  
30 Diesel Particulate Emission Control' SAE paper 890404, 1989 and US patent specification 4 902 487 (1990) which is based on the work which is discussed in the paper, discuss the reaction between nitrogen dioxide (NO<sub>2</sub>) and particulate carbon present in diesel engine exhaust gases  
35 at temperatures in the region of 265°C to oxidise the

- 3 -

carbonaceous particulates to carbon monoxide and carbon dioxide and nitric oxide (NO) from the reduction of the NO<sub>2</sub>. Although nitric oxide is produced from the oxidation of carbon by nitrogen dioxide this reaction also has a pathway for the production of nitrogen as well as nitric oxide that is highlighted in US patent specification 4 902 487 (1990) by Cooper et al. In particular, there is discussed the use of a platinum based catalyst to oxidise NO initially present in the exhaust gases to NO<sub>2</sub>. Particulate carbon which is not also oxidised by the platinum catalyst is collected on a soot trap, for example a ceramic honeycomb. NO<sub>2</sub> then adsorbs onto the trapped particulates and oxidises the trapped particulate carbon. It is suggested also that the oxidation rate can be enhanced by the presence of water adsorbed on the material of the soot trap, and that the presence of a carbon combustion catalyst derived from an alkali metal salt such as lithium nitrate can lower the temperature required for the combustion of carbon in the presence of nitrogen dioxide. The use of alkali metal salts as combustion catalysts also is described in patent specification GB 2 232 613 B.

However, Cooper et al state that a problem which arises with the use of the NO<sub>2</sub>/carbon reaction catalysed by platinum-based catalysts is that the platinum based catalyst is not selective. That is it also oxidises any sulphur dioxide which may be present in the exhaust gases (derived from sulphur compounds present in the fuel) into sulphuric acid particulates. They state that the total conversion of sulphur dioxide derived from 500 ppm sulphur in the fuel, will result in a total particulate emission which is five times higher than that permitted by legislation current in 1994, and even more so under

- 4 -

proposed legislation.

Recently, PSA Peugeot Citroen has disclosed the use of Eolys, a cerium oxide-based additive for diesel fuel that is injected from an additional tank at the rear of the vehicle into the diesel tank. The Eolys reduces the temperature at which carbonaceous particulates trapped on a filter combust from 550°C to 450°C. The Eolys reagent is used in conjunction with a post-combustion phase fuel injection that raises the exhaust gas temperature by 200-250°C and an oxidation catalyst before the trap that increases the exhaust temperature by a further 100°C to between 450-500°C allowing regeneration to take place (FT Automotive Environment Analyst, Issue 52, May 1999, page 27, EP 0 488 831, EP 0 661 429, FR 2668203).

It is an object of the present invention to provide a method for promoting the selective oxidation of NO in an internal combustion engine exhaust gas stream to NO<sub>2</sub> to facilitate the removal of particulate carbonaceous combustion products from internal combustion engine exhaust gases, which is tolerant to the presence of sulphur compounds in the exhaust gas stream.

According to the present invention there is provided a method of producing nitrogen dioxide from nitric oxide contained in a gaseous medium, comprising the operation of subjecting the gaseous medium to the action of a non-thermal plasma. The nitrogen dioxide thus produced is utilised to oxidise carbon. Any nitric oxide produced in this reaction together with any residual nitrogenous oxide in the exhaust gases that is not initially converted in the non-thermal plasma to nitrogen dioxide is then reduced to nitrogen. Nitric oxide derived from the reaction of carbon with nitrogen dioxide, which is

- 5 -

produced in the fuel combustion process and not by selective oxidation in a plasma, thus also undergoes reduction to nitrogen according to the present invention.

5       A non-thermal plasma is a plasma in which the majority of the electrical energy input goes into the production of energetic electrons and is characterised by high electron mean energies while the gas remains at near ambient temperature and pressure (BM Penetrante, 'Power  
10 consumption of non-thermal plasma reactors' in Emerging Technologies in Hazardous Waste Management VI, American Chemical Society, September 19-21, 1994, Page 195).

      The non-thermal plasma can be generated in a number  
15 of ways, for example it can be generated in a packed ferroelectric bed reactor similar to that described in specification GB 2 274 412, a pulsed corona discharge reactor, a silent electric discharge reactor (also known as a dielectric barrier reactor), a dielectric barrier  
20 reactor filled with a bed of gas permeable dielectric material, or a surface discharge reactor.

      Non-thermal plasma reactors have been known for a considerable time. For example dielectric barrier  
25 reactors have been used for over a hundred years, described initially by W von Siemens to produce ozone (Annalen der Physik und Chemie, volume 102, 66-122, 1857). The Siemens tube consisted of a narrow annular discharge gap between two coaxial glass cylinders. A  
30 'silent discharge' was established by applying an alternating high voltage through the glass walls. Air or oxygen passing through the discharge was partially converted into ozone. Widespread use of dielectric barrier discharges began at the beginning of the 20<sup>th</sup>  
35 century when large scale application to water purification using ozone was introduced in several cities

including Nice (1907) and St Petersburg (1910). Several fundamental studies on these reactors at this time were described by for example E Warburg, Annalen der Physik, volume 9, 781, 1902, E Warburg, Annalen der Physik, 5 volume 13, 464, 1904 and E Warburg, Annalen der Physik, volume 17, 1, 1905. High specific energy devices (high power deposited per unit gas flow) were soon developed. Thus E Warburg and G. Leithauser, Annalen der Physik, volume 20, 734-750, 1906; V. Ehrlich and F. Russ, 10 Monatshefte fur Chemie und Teihe anderen Wissenschaften, volume 22, 917-998, 1911.

Non-thermal plasma reactors such as dielectric barrier discharge reactors have also been used for other 15 applications in plasma chemistry. These include synthesis of inorganic and organic compounds, generation of excimers to produce ultra violet radiation, detoxification of hazardous wastes such as volatile organic compounds and the removal of nitrogen and sulphur 20 oxides from the flue gases of large scale burning processes. Modern ozone generators have been described by Kogelschatz (Proceedings of the 10<sup>th</sup> International Conference on Gas Discharges and their Applications, 1992) while a reactor for the remediation of volatile 25 organic compounds is described by Evans et al (Journal of Applied Physics, volume 74, 5378-5386, 1993). Treatment of nitrogen oxides in a dielectric barrier discharge reactor is described by McLarnon and Penetrante (Society of Automotive Engineers paper 98-2434, October 1998).

30

According to the invention in one aspect there is provided a method of removing nitrogenous oxides and carbonaceous particulates from the exhaust gases from an internal combustion engine supplied with a combustion 35 fuel, which method comprises the operations of passing the exhaust gases through a reactor chamber, the exhaust



- 7 -

gases containing hydrocarbon either added separately or residually derived from said combustion fuel, exciting a non-thermal plasma therein, characterised by utilising nitrogen dioxide produced in the exhaust gases by the action of the non-thermal plasma upon nitric oxide contained in the exhaust gases to oxidise the carbonaceous particulates contained in the exhaust gases. Preferably there is included the step of reducing to nitrogen any nitric oxide produced by the oxidation of the carbonaceous particulates together with any nitric oxide remaining in the exhaust having not been converted to nitrogen dioxide in the plasma. While it is generally understood that oxidation of nitric oxide to nitrogen dioxide in a non-thermal plasma is enhanced in the presence of a hydrocarbon in the gaseous phase (see B.M. Penetrante et al, Paper number SAE 982508, 1988, Figure 2) the hydrocarbon may be that which is present in the exhaust gases from the fuel combustion processes or be added separately to the exhaust gases to enhance the selective oxidation reaction to nitrogen dioxide. The hydrocarbon may be in the form of the fuel as described in our publication WO 99/12638 published on 18 March 1999.

The  $\text{NO}_2$  produced in the plasma is adsorbed on the particulate carbon with which it reacts to produce carbon monoxide, carbon dioxide, nitrogen and  $\text{NO}$ .

Preferably, the oxidation of the carbonaceous particulates is facilitated by passing the excited exhaust gases through a filter element in which the particulate carbon becomes trapped. The filter element may be contained either in or outside the plasma forming region and may be ceramic material or, alternatively when outside the plasma forming region, may be metallic or

- 8 -

polymeric The filter element can be in the form of spheres, pellets, extrudates, fibres, sheets, coils, granules, foams or honeycomb monolith. Combinations of one or more of the above can be used to create a filter structure with a non-uniform surface area and porosity, for example a graded porosity, when presented to the exhaust gas. The filter element may contain a coating of, be impregnated with or generally treated by for example ion exchange or doping or be made out of a carbon combustion catalyst for example cerium oxide or alkali metal doped lanthanum oxide-vanadium pentoxide or perovskite as described in our publication WO99/38603 published on 5 August 1999 to aid the regeneration of the filter. The fuel supplied to the internal combustion engine from which the exhaust gases come may contain a chemical additive for aiding combustion of carbonaceous particulates by nitrogen dioxide. In this case the additive, or a derivative of it formed on fuel combustion is present in the exhaust gases as they pass through the plasma. The chemical additive may be added separately and not be part of the fuel. The presence of a combustion catalyst in the fuel or on the filter can reduce the concentration of nitrogen dioxide required to be produced in the exhaust gases by the non-thermal plasma and aid efficiency. The temperature of the exhaust gases can be raised in a post-combustion phase through the combustion of additional fuel so as to raise the temperature of the filter, aid the regeneration of the filter and limit the power requirements for the generation of the plasma. The temperature of the exhaust gases can also be raised by the exothermic reactions on an oxidation catalyst.

The resultant gas stream can then be mixed with a reductant such as a hydrocarbon vapour for example propene ( $C_3H_6$ ), passed through a second non-thermal plasma

- 9 -

reactor and then over a catalyst, such as a metal-doped zeolite, which acts to reduce the NO to nitrogen; a non-zeolite catalyst such as alumina can be used. The catalyst may be present in the plasma zone of the second reactor but can also be outside of the plasma zone and can be in the form of spheres, pellets, extrudates, fibres, sheets, coils, granules, foams, honeycomb monolith or as a coating on a foam or honeycomb monolith. Combinations of one or more of the above can be used to create a structure with a non-uniform surface area and porosity, for example a graded porosity, when presented to the exhaust gas. Foams and monoliths can be ceramic, metallic or polymeric and examples of foams and monoliths include but are not limited to alumina, zirconia, titania, zeolite for foams and cordierite, alumina, zeolite and Fecralloy metal for honeycomb monoliths. The second plasma serves one or more or a combination of the following functions, the importance of which is subject to the choice of zeolite, metal dopant, dopant loading and other such factors when the catalyst is a zeolite that can be metal-exchanged, metal-doped or in the H-form. Namely, (1) the 'activation' of the hydrocarbon. The term activation has been described in our publication WO99/12638 filed on 26 August 1998. Thus by activated hydrocarbon we mean plasma activated hydrocarbon in which the activity of the hydrocarbon has been enhanced in a plasma by for example partial oxidation, free radical formation, ionisation and/or energy absorption (e.g. into vibrational or rotational modes). (2) the selective oxidation of NO to NO<sub>2</sub> and (3) the conversion of 'residual' soot that is particulate carbon to useful gas phase hydrocarbon reductant. Material that may not be catalytic for the reduction of nitrogeneous material when not exposed to a plasma may develop catalytic properties for this reduction when exposed to a plasma due for

- 10 -

example to activation by O atoms. The catalyst may enhance the effect hydrocarbon has on the oxidation of nitrogeneous oxide to nitrogen dioxide when the catalyst and hydrocarbon are in a plasma region. The catalyst, when  
5 in a plasma zone, may activate carbonaceous material. A reductant other than hydrocarbon may be used, in particular nitrogen containing species such as ammonia, urea, ammonium carbonate or cyanuric acid. When a nitrogen containing species is used as a reductant for  
10 nitrogeneous oxide reduction a particularly useful catalyst is vanadium pentoxide-titanium dioxide. When using a nitrogen containing reductant species, mixing with effluent can be made after the effluent has passed through the plasma forming region of the second reactor  
15 before contact with the catalyst.

According to the invention in another aspect there is provided a reactor system for removing nitrogenous oxides and particulate carbon combustion products from  
20 the exhaust emissions of internal combustion engines, comprising a first reactor chamber including means for establishing a non-thermal plasma therein into which hydrocarbon vapour or gas can be added in addition to any hydrocarbon vapour or gas present in the exhaust gases  
25 from the fuel combustion processes, a trap for carbonaceous particulates, means for passing the effluent from the first reactor chamber through the carbonaceous particulate trap that may be in or outside of the plasma zone, means for mixing the effluent from the carbonaceous  
30 particulate trap with a reductant that is either hydrocarbon or nitrogen containing species such as ammonia and passing the mixture through a second reactor chamber including means for establishing a non-thermal plasma therein and means for passing the activated  
35 mixture over a catalyst adapted to reduce nitric oxide to nitrogen. The catalyst may be in or outside of the

- 11 -

plasma forming region and the reductant may be mixed with the effluent from the first reactor chamber after this effluent has passed through the plasma zone of the second reactor before contact with the catalyst.

5

Preferably, the plasma excited in the second reactor chamber also is of the non-thermal type.

The means for establishing non-thermal plasmas in one, other or both of the reactor chambers may comprise a bed of gas permeable high dielectric and/or ferroelectric material contained between two electrodes, means for establishing a pulsed corona discharge in the reactor chamber concerned, means for establishing a silent electric discharge in the reactor chamber concerned, the combination of means for establishing a silent electric discharge with a gas permeable bed of dielectric material, or means for establishing a surface electric discharge in the reactor chamber concerned.

20

A suitable catalyst for the reduction of nitrogenous oxides such as nitric oxide to nitrogen is an alkali metal exchanged zeolite Y, or silver aluminate. Other metal-exchanged or metal-doped zeolite material such as that known as Cu/ZSM-5, Fe/ZSM-5 or Co/ZSM-5 with or without catalyst promoting cations of cerium or lanthanum, zeolite beta, hydrogen exchanged zeolites such as H-ZSM-5 are also suitable materials. Other suitable materials for the reduction of nitrogenous oxides to nitrogen are aluminas including alpha, gamma, chi and other crystalline phases, oxides of titanium, zirconium, cerium and vanadium, perovskites, spinels and mixtures of these materials. Metal doped inorganic oxides such as cobalt-doped aluminas are also suitable materials.

Vanadium pentoxide-titanium dioxide is a particularly suitable catalyst when the reductant is a nitrogen

- 12 -

containing species. Catalyst can however trap and activate the trapped carbon even when not in a plasma.

The invention will now be described, by way of  
5 example, with reference to the accompanying drawing which is a longitudinal section of a schematic system embodying the invention for removing nitrogenous oxides and particulate carbonaceous combustion products from the exhaust emissions from internal combustion engines.

10

Referring to the drawing, a reactor system 100 for removing nitrogenous oxide and particulate carbon combustion products from the exhaust gases from internal combustion engines comprises, a first reactor 101 And a  
15 second reactor 102 in series with the first reactor, 101.

The first reactor 101 has an inlet stub 103 and the second reactor 102 has an outlet stub 104 by means of which the reactor 100 can be incorporated into the  
20 exhaust system of an internal combustion engine which is not shown in the drawing. Inside the reactor 101 is a chamber 105 which contains a means 106 for generating a plasma in exhaust gases entering the reactor 101 and a second chamber 107 containing a ceramic particulate  
25 filter bed 108. The particulate filter bed may also be contained in the plasma region thus avoiding the requirement for a second chamber. In addition an inlet 121 is available for introducing additional hydrocarbon into the exhaust when insufficient residual hydrocarbon  
30 is present from the combustion fuel. The plasma generating means 106 is not shown in detail because it can take a number of forms. For example it can be a pellet bed device such as that disclosed in our patent GB 2 274 412, a pulsed corona discharge device such as that  
35 disclosed in our patent GB 2 282 738, a silent electric discharge producing device, a silent electric discharge

- 13 -

device in association with a gas permeable bed of dielectric material, or a device for producing a surface electric discharge in the chamber 105 of the reactor 100. If the plasma-generator 106 is a pellet bed, or similar  
5 device, then a proviso is that the material of the pellet bed, or similar should not be made of a material which acts to reduce higher oxides of nitrogen. A flow-smoothing baffle 109 is positioned between the chambers 105, 107 of the reactor 101. If the plasma generator 106  
10 is of a type which incorporates a gas permeable bed of dielectric material to assist the generation of a plasma in the exhaust gases passing through the chamber 105, then its porosity should be such as to minimise the trapping of particulate carbonaceous combustion products  
15 in it.

The second reactor, 102, also is divided into two chambers 110 and 111. The chamber 110 contains a plasma generator 112, which can be any of the types of plasma  
20 generator mentioned above, and the chamber 111 contains a permeable bed 113 of a catalyst adapted to reduce nitrogenous oxide to nitrogen. Again, a flow smoother 114 is provided between the chambers 110, 111 of the reactor 102. A suitable catalyst is an alkali metal-  
25 exchanged zeolite Y or silver aluminate. Other metal-exchanged or metal doped zeolite material such as those known as Cu/ZSM-5, Fe/ZSM-5, Co/ZSM-5, zeolite beta and hydrogen exchanged zeolites such as H-ZSM-5 are suitable materials. Other suitable materials for the reduction of  
30 nitrogenous oxides to nitrogen are aluminas including alpha, gamma, chi and other crystalline phases, oxides of titanium, zirconium, cerium and vanadium, perovskites, spinels and mixtures of these materials. Metal doped inorganic oxides such as cobalt-doped aluminas are also  
35 suitable materials. Vanadium pentoxide-titanium dioxide is a particularly suitable catalyst when a nitrogen

- 14 -

containing reductant is used to replace hydrocarbon reductant. Catalyst can also be present in the second plasma region as a bed of spheres, pellets, extrudates, fibres, sheets, coils, granules, foams, honeycomb  
5 monolith or as a coating on a foam or honeycomb. Combinations of one or more of the above can be used to create a structure with a non-uniform surface area and porosity when exposed to the exhaust gas. Foams and monoliths can be ceramic, metallic or polymeric.

10

Upstream of the plasma generator 112 is a port 115 through which a gaseous hydrocarbon or nitrogen containing reductant can be added to the effluent from the reactor 101. We have described in our publication  
15 WO99/05400 filed on 13 July 1998 the close proximity of a reactor bed and power supply unit both housed in an electrically conducting enclosure and this arrangement is particularly suitable for the present invention.

20

The system operates as follows:

Exhaust gases containing a mixture of nitrogen oxides and particulate carbonaceous combustion products pass through the plasma generator 106 in which NO  
25 contained in the exhaust gases is oxidised to NO<sub>2</sub> and this oxidation is enhanced by the presence of hydrocarbon in the exhaust from uncombusted fuel or additional hydrocarbon added to the exhaust. The NO<sub>2</sub> then oxidises carbon particulates trapped in the ceramic filter bed 108  
30 to CO and CO<sub>2</sub>, being itself reduced to NO and N<sub>2</sub> in the process. The presence of a combustion catalyst in the fuel, injected separately or on the filter can reduce the requirements for nitrogen dioxide for regeneration of the filter and aid efficiency. The effluent from the reactor  
35 101 containing nitrogenous oxide from the exhaust that



- 15 -

was not oxidised in the plasma to nitrogen dioxide and nitric oxide from the reaction of nitrogen dioxide with carbon is then mixed with the hydrocarbon, which can be the fuel used to run the engine, or additional

5 hydrocarbon such as propene ( $C_3H_6$ ), and the mixture is passed through the second plasma generator 112 in which activated hydrocarbons are produced. The term activated hydrocarbons has been defined above. These then react on the catalyst, which can be a zeolite, in the bed 113 to  
10 reduce the nitrogenous oxide in the exhaust gases to  $N_2$ . The effluent from the reactor 101 can be mixed with a nitrogen containing reductant instead of hydrocarbon although nitrogen containing reductant can be mixed with the exhaust after the latter has passed through the  
15 second reactor and before contact with a catalyst. Catalyst can also be present in the second plasma region as spheres, pellets, extrudates, fibres, sheets, coils, granules, foams, honeycomb monolith, or as a coating on a foam or honeycomb.

20

Unlike the oxidising catalysts used hitherto, the non-thermal plasmas produced in the chambers 105 and 110 of the reactor 100 carry out the oxidation of the NO to  $NO_2$  and the activation of the hydrocarbons without  
25 effecting the oxidation of any sulphur compounds to  $SO_2$ , which could combine with water in the exhaust gases to produce sulphuric or sulphurous acids. Other arrangements by which exhaust from the first reactor can be mixed with hydrocarbon for treatment in the second  
30 reactor are described in Figure 8 of our publication WO99/12638.

Claims

1. A method of removing nitrogenous oxides and carbonaceous particulates from the exhaust gases from an  
5 internal combustion engine supplied with a combustion fuel, which method comprises the operations of passing the exhaust gases through a reactor chamber, the exhaust gases containing hydrocarbon either added separately or residually derived from said combustion fuel, exciting a  
10 non-thermal plasma therein, characterised by utilising nitrogen dioxide produced in the exhaust gases by the action of the non-thermal plasma upon nitric oxide contained in the exhaust gases to oxidise the carbonaceous particulates contained in the exhaust gases.  
15
2. A method according to claim 1, further characterised in that subsequent to the initial non-thermal plasma being excited in the exhaust gases, the exhaust gases are passed through a filter (108) adapted to trap the  
20 carbonaceous particulates thereby to facilitate the oxidation of the carbonaceous particulates.
3. A method according to claim 1, further characterised in that there is included the step of reducing to  
25 nitrogen gas nitrogen monoxide produced as a result of the oxidation of the carbonaceous particulates by nitrogen dioxide as well as any nitric oxide remaining in the exhaust gases having not been converted to nitrogen dioxide in the non-thermal plasma.  
30
4. A method according to claim 2, further characterised in that the filter (108) is present in or outside of the plasma-forming region.
- 35 5. A method according to claim 4, further characterised in that the filter (108) is made of a ceramic material,

- 17 -

or where the filter (108) is outside of the plasma forming region, ceramic, metallic or polymeric material.

6. A method according to claim 5, further characterised in that the filter (108) adapted to trap the carbonaceous particulates contains a coating of, is impregnated with or is made of, a carbon combustion catalyst.

7. A method according to claim 6, further characterised in that the carbon combustion catalyst is cerium oxide or alkali metal doped lanthanum oxide-vanadium pentoxide.

8. A method according to claim 1, further characterised in that the fuel contains a carbon combustion catalyst.

9. A method according to any of the preceding claims, further characterised in that subsequent to the reaction of the nitrogen dioxide with the carbonaceous particulates the exhaust gases are mixed with a reductant vapour, a non-thermal plasma is generated in the mixture and the excited mixture is contacted with a catalyst adapted to reduce nitrogen monoxide to nitrogen.

10. A method according to claim 9, further characterised in that the reductant is hydrocarbon in the fuel or added hydrocarbon.

11. A method according to claim 10, further characterised in that the reductant is added hydrocarbon comprising propene.

12. A method according to claim 9, further characterised in that the reductant is a nitrogen containing species.

13. A method according to claim 12 wherein the nitrogen containing species is ammonia, urea, ammonium carbonate

- 18 -

or cyanuric acid.

14. A method according to any one of claims 9, 11, 12 and 13, further characterised in that the reductant  
5 species is added to exhaust gas from the reaction of nitrogen dioxide and carbonaceous particulates after this exhaust gas is contacted with a second non-thermal plasma and before contact with the catalyst.
- 10 15. A method according to claim 9 or claim 10, further characterised in that the catalyst for reducing nitrogen monoxide is a metal-doped zeolite or hydrogen-exchanged zeolite, an oxide of aluminium, titanium, zirconium,  
15 cerium or vanadium, or a perovskite, spinel or mixture thereof.
16. A method according to any one of claims 9, 10, 11 and 12, further characterised in that the catalyst for  
20 reducing nitrogen monoxide comprises vanadium pentoxide-titanium dioxide.
17. A reactor system for removing nitrogenous oxides and particulate carbon combustion products from the exhaust  
25 emissions of internal combustion engines, comprising a first reactor chamber (105) including means (106) for establishing a non-thermal plasma therein, characterised by a trap (108) for carbonaceous particulates, means for passing the effluent from the first reactor chamber  
30 through the carbonaceous particulate trap (108), means for mixing the effluent from the carbonaceous particulate trap (108) with a hydrocarbon or nitrogen containing species and passing the mixture through a second reactor chamber (110) including means (112) for establishing a non-thermal plasma therein and means for passing the  
35 activated mixture over a catalyst (113) adapted to reduce nitric oxide to nitrogen.

- 19 -

18. A reactor system for removing nitrogenous oxides and particulate carbon combustion products from the exhaust emissions of internal combustion engines, comprising a  
5 first reactor chamber (105) including means (106) for establishing a non-thermal plasma therein, characterised by a trap (108) for carbonaceous particulates, means for passing the effluent from the first reactor chamber through the carbonaceous particulate trap (108) and  
10 passing the mixture through a second reactor chamber (110) including means (112) for establishing a non-thermal plasma therein, means for mixing the effluent from the second reactor chamber (110) with a nitrogen containing species and means for passing the activated  
15 mixture over a catalyst (113) adapted to reduce nitric oxide to nitrogen.

19. A system according to claim 17 or claim 18, further characterised in that the means (106;112) for  
20 establishing non-thermal plasmas in internal combustion engine exhaust gases passing through the reactor chambers (105;110) is selected from the group comprising, a gas permeable bed of ferroelectric material contained between two electrodes one of which is a high-voltage input  
25 electrode; means for establishing a corona discharge in the reactor chamber concerned; means for establishing a silent electric discharge in the reactor chamber concerned; means for establishing a surface electric discharge in the reactor chamber concerned; and the  
30 combination of means for establishing a silent electric discharge in the reactor chamber concerned and gas permeable bed of ferroelectric material.

20. A system according to claim 17 or 18, further  
35 characterised in that the trap (108) for carbonaceous particulates may be positioned in or outside of the

- 20 -

plasma forming region of the first reactor chamber (105).

21. A system according to claim 20, further characterised in that the trap (108) is made of a ceramic material or, where the trap (108) is outside of the plasma forming region, of ceramic, metallic or polymeric material.

22. A system according to claim 17, further characterised in that an inlet (121) is provided for separately introducing hydrocarbon vapour or gas prior to passage of the exhaust gases through the plasma forming region (106) of the first reactor chamber (105), said separately introduced hydrocarbon vapour or gas being in addition to any which may be present in the exhaust gases from the combustion fuel.

23. A system according to claim 17 further characterised in that the second reactor chamber (110) has two compartments in the upstream compartment of which there is included means (112) for establishing a non-thermal plasma in internal combustion engine exhaust gases passing through the reactor and in the second compartment of which there is contained a gas permeable body (113) of a material adapted to catalyse the reduction of nitrogen monoxide to nitrogen and there is included a port (115) by means of which a hydrocarbon gas or vapour can be added to the effluent from the first reactor chamber (105) prior to its being passed through the region of the first compartment of the second reactor chamber (110) containing the means (112) for generating a non-thermal plasma in the mixture.

24. A system according to claim 17 or claim 18, further characterised in that the catalyst is a metal-doped zeolite.

- 21 -

25. A system according to claim 17 or claim 18, further characterised in that the catalyst is a metal-doped zeolite known as Cu/ZSM-5 or Fe/ZSM-5 or Co/ZSM-5, or an  
5 alkali metal-exchanged zeolite Y, zeolite beta or silver aluminate or hydrogen exchanged zeolite or oxide of aluminium, titanium, zirconium, cerium and vanadium, or a perovskite, spinel or a mixture thereof.

10 26. A system according to claims 24 or claim 25, further characterised in that the catalyst is present in the second reactor chamber (110) in the form of spheres, pellets, extrudates, fibres, sheets, coils, granules,  
15 foam or honeycomb monolith or as a coating on a ceramic foam or ceramic honeycomb.

27. A system according to claim 26, further characterised in that the catalyst is present in the plasma forming region (112) of the second reactor chamber  
20 (110).

28. A system according to claim 26, further characterised in that the catalyst is placed outside of the plasma forming region (112).  
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